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(54) **PROCESS FOR THE HYDROGENATION OF IMINES**

VERFAHREN ZUR HYDRIERUNG VON IMINEN

PROCEDE D'HYDROGENATION D'IMINES

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WO-A-95/21176
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US-A- 5 371 256

EP 0 842 140 B1

Description

[0001] The present invention relates to a process for the preparation of amines by hydrogenation of imines in the presence of dinuclear iridium complexes having ferrocenyl(di-tertiary phosphine) ligands.

[0002] US-A-5 112 999 describes dinuclear Ir(III) complexes having ditertiary diphosphine ligands and halide bridges, halide and hydride ligands and Ir(III) halide complex salts containing a ditertiary diphosphine ligand that are suitable as catalysts for a hydrogenation of imines that may be an enantioselective hydrogenation. Ditertiary ferrocenyldiphosphine ligands are not mentioned. US-A-5 371 256 and EP-A-0 612 758 describe iridium complexes having chiral ferrocenyldiphosphine ligands for the homogeneous enantioselective hydrogenation of imines. Those homogeneous catalysis processes have proved valuable, but the activity and selectivity of the catalysts, while already high *per se,* are still not entirely satisfactory. It has also been suggested that soluble halides be added to the reaction mixture in order to improve the enantioselectivity and the activity and stability of the catalysts.

[0003] It has now been found that dinuclear Ir(III) complexes having ditertiary diphosphine ligands and halide bridges, halide and hydride ligands and Ir(III) halide complex salts containing a ditertiary diphosphine ligand exhibit an unexpectedly high catalyst activity and stability in the hydrogenation of imines, on their own, without further additives. Furthermore, when chiral diphosphine ligands and prochiral imines are used, extraordinarily high enantioselectivities are achieved, which may amount to an enantiomeric excess of 80% and more. The reaction times for a one hundred percent conversion may even be considerably less than an hour and, even at low catalyst concentrations, very high yields can still be achieved in relatively short reaction times.

[0004] The present invention relates to a process for the preparation of primary or secondary amines by hydrogenation of imines with hydrogen at elevated pressure and in the presence of a dinuclear Ir(III) complex having ditertiary diphosphine ligands, halide bridges, halide and hydride ligands, or an Ir(III) halide complex salt containing ditertiary diphosphine ligands, as catalyst, wherein the catalyst corresponds to formula I or Ia or to mixtures of at least two compounds of formula I, at least two compounds of formulae I and Ia, or at least two compounds of formula Ia

$$[(DIP)IrX_qY_r]_2 \quad (I),$$

$$[(DIP)X_4]^{\ominus}Me^{\oplus} \quad (Ia),$$

wherein

DIP is the ditertiary diphosphine ligand of a ferrocenyldiphosphine the phosphine groups of which are either bonded directly or *via* a bridge group $-CR_vR_w-$ to the ortho positions of a cyclopentadienyl ring or are each bonded to a cyclopentadienyl ring of a ferrocenyl, so that a 5-, 6- or 7-membered ring is formed together with the Ir atom;
R_v and R_w are each independently of the other hydrogen, C_1-C_8alkyl, C_1-C_4fluoroalkyl, phenyl or benzyl, or are phenyl or benzyl each having from 1 to 3 C_1-C_4alkyl or C_1-C_4-alkoxy substituents;
X is Cl, Br or I;
Y is H;
q is the number 2 or 3 and r is 0 or 1, the sum of q+r being equal to 3; and
$Me^{\oplus}$ is an alkali metal cation or quaternary ammonium.

[0005] The iridium compounds are preferably homogeneous catalysts that are to a large extent soluble in the reaction medium. The term "catalyst" also includes catalyst precursors which are converted into an active catalyst species at the beginning of a hydrogenation reaction.

[0006] R_w is preferably hydrogen. R_v is preferably C_1-C_4alkyl, for example methyl, ethyl, n-propyl or n-butyl, and especially methyl.

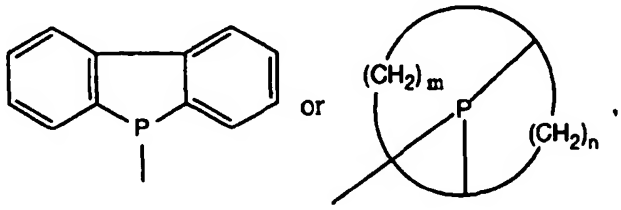
[0007] The ditertiary ferrocenyldiphosphine preferably contains at least one chiral group, and the diphosphine is especially an optically pure stereoisomer or a pair of diastereoisomers since, with catalysts that contain chiral ligands, optical inductions are obtained in asymmetric hydrogen reactions.

[0008] The phosphine groups preferably contain two identical or different, more preferably identical, unsubstituted or substituted hydrocarbon radicals having from 1 to 20, especially from 1 to 12, carbon atoms. Preferred diphosphines are those wherein the secondary phosphine groups contain two identical or different radicals from the following group: linear or branched C_1-C_{12}alkyl; unsubstituted or C_1-C_6alkyl- or C_1-C_6alkoxy-substituted C_5-C_{12}-cycloalkyl, C_5-C_{12}cycloalkyl-CH_2-, phenyl and benzyl; and phenyl and benzyl each substituted by halogen, (e.g. F, Cl and Br), C_1-C_6haloalkyl, $(C_1$-C_{12}alkyl$)_3Si$, $(C_6H_5)_3Si$, C_1-C_6haloalkoxy (e.g. trifluoromethoxy), $-NH_2$, phenyl$_2$N-, benzyl-, morpholi-

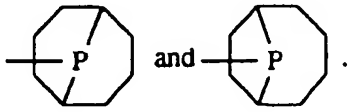
nyl, piperidinyl, pyrrolidinyl, $(C_1$-C_{12}alkyl$)_2N$-, -ammonium-$X_1^{\ominus}$-, $-SO_3M_1$, $-CO_2M_1$, $-PO_3M_1$ or by -COO-C_1-C_6alkyl (e. g. $-COOCH_3$); wherein M_1 is an alkali metal or hydrogen and $X_1^{\ominus}$ is the anion of a monobasic acid. M_1 is preferably H, Li, Na or K. $A_1^{\ominus}$, as the anion of a monobasic acid, is preferably $Cl^{\ominus}$, $Br^{\ominus}$ or the anion of a carboxylic acid, for example formate, acetate, trichloroacetate or trifluoroacetate.

[0009] Examples of alkyl that preferably contains from 1 to 6 carbon atoms are methyl, ethyl, n-propyl, isopropyl, n-, iso- and tert-butyl and the isomers of pentyl and hexyl. Examples of unsubstituted or alkyl-substituted cycloalkyl are cyclopentyl, cyclohexyl, methyl- or ethyl-cyclohexyl and dimethylcyclohexyl. Examples of phenyl and benzyl each substituted by alkyl, alkoxy or by haloalkoxy are methylphenyl, dimethylphenyl, trimethylphenyl, ethylphenyl, methylbenzyl, methoxyphenyl, dimethoxyphenyl, trifluoromethylphenyl, bistrifluoromethylphenyl, tristrifluoromethylphenyl, trifluoromethoxyphenyl and bistrifluoromethoxyphenyl. Preferred phosphine groups are those which contain identical or different, preferably identical, radicals from the following group: C_1-C_6alkyl; cyclopentyl and cyclohexyl that are unsubstituted or have from one to three C_1-C_4alkyl or C_1-C_4alkoxy substituents; and benzyl and especially phenyl that are unsubstituted or have from one to three C_1-C_4alkyl, C_1-C_4alkoxy, F, Cl, C_1-C_4fluoroalkyl or C_1-C_4fluoroalkoxy substituents.

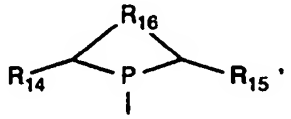
[0010] The secondary phosphine groups bonded to the cyclopentadienyl may be radicals of the formula



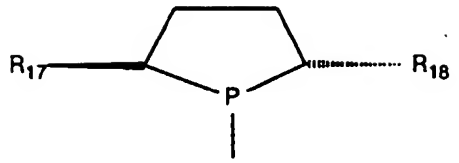
wherein m and n are each independently of the other an integer from 2 to 10 and the sum of m+n is equal to from 4 to 12, especially from 5 to 8. Examples thereof are [3.3.1]- and [4.2.1]-phobyl of the formulae



[0011] The secondary phosphine groups may also be radicals of the formula



wherein R_{16} is C_1-C_4alkylene, preferably C_2- or C_3-alkylene, and R_{14} and R_{15} are each independently of the other hydrogen, C_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6haloalkyl, C_5- or C_6-cycloalkyl, or phenyl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or by halogen, or benzyl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloatkyl or by halogen. R_{14} and R_{15} may be, for example, methyl, ethyl, n- or iso-propyl, n-, iso- or tert-butyl, cyclohexyl, phenyl or benzyl. Halogen is preferably F or Cl. Those phosphine groups possess further chiral carbon atoms and can be used in the form of racemates or diastereoisomers. Among those phosphine ligands, those of the formula



wherein R_{17} and R_{18} are C_1-C_4alkyl or phenyl, are especially preferred.

[0012] The ferrocenyldiphosphine preferably corresponds to formula II

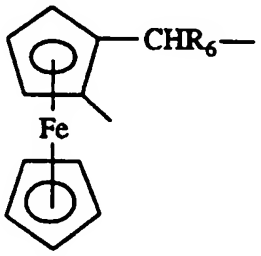
$$R_1R_2P\text{-}R_5\text{-}PR_3R_4 \qquad \text{(II)},$$

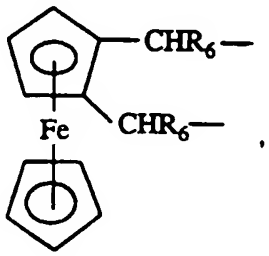
wherein

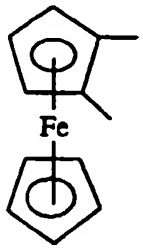
R_1, R_2, R_3 and R_4 are each independently of the others a hydrocarbon radical having from 1 to 20 carbon atoms that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6alkoxy, halogen, C_1-C_6haloalkyl, $(C_1\text{-}C_{12}alkyl)_3Si$, $(C_6H_5)_3Si$, C_1-C_6haloalkoxy, $-NH_2$, $phenyl_2N$-, $benzyl_2N$-, morpholinyl, piperidinyl, pyrrolidinyl, $(C_1\text{-}C_{12}alkyl)_2N$-, -ammonium-$X_1^{\ominus}$, $-SO_3M_1$, $-CO_2M_1$, $-PO_3M_1$ or by -COO-C_1-C_6alkyl, wherein M_1 is an alkali metal or hydrogen and $X_1^{\ominus}$ is the anion of a monobasic acid;

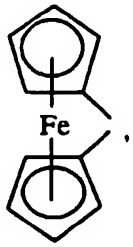
R_1 and R_2 together and R_3 and R_4 together form a C_1-C_4alkylene radical that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6haloalkyl, C_5- or C_6-cycloalkyl, by phenyl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or by halogen, or by benzyl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or by halogen; and

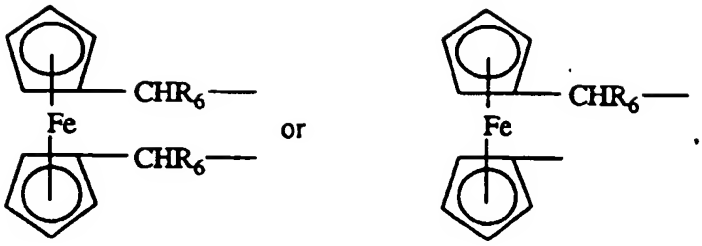
R_5 is a radical of the formula







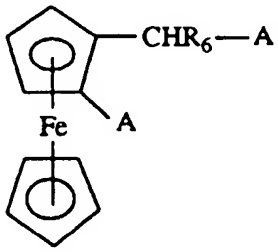




wherein
R_6 is hydrogen, C_1-C_8alkyl, C_1-C_4fluoroalkyl, phenyl or phenyl having from 1 to 3 C_1-C_4-alkyl or C_1-C_4alkoxy substituents.

[0013] R_1, R_2, R_3 and R_4 are preferably identical or different, preferably identical, radicals from the following group: C_1-C_6alkyl; cyclopentyl and cyclohexyl that are unsubstituted or have from one to three C_1-C_6alkyl or C_1-C_6alkoxy substituents; and benzyl and especially phenyl that are unsubstituted or have from one to three C_1-C_4alkyl, C_1-C_4alkoxy, F, Cl, C_1-C_4fluoroalkyl or C_1-C_4fluoroalkoxy substituents.

[0014] Especially suitable disphosphine ligands DIP are those of formula III



(III),

wherein

R_6 is hydrogen and especially methyl; and
A represents identical or different groups $-P(R)_2$ wherein R is C_1-C_6alkyl, cyclohexyl, phenyl, benzyl, or phenyl or benzyl each having from one to three C_1-C_4alkyl, disubstituted amino, C_1-C_4alkoxy, $-CF_3$ or partially or completely fluorinated C_1-C_4alkoxy substituents.

[0015] R, when alkyl, is preferably branched C_3-C_6alkyl. Disubstituted amino is preferably secondary amino having from 2 to 20, and preferably from 2 to 12, carbon atoms. It may have the formula $-NR_7R_{07}$ wherein R_7 and R_{07} are each independently of the other C_1-C_6-alkyl, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_5- or C_6-cycloalkyl, or unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted phenyl or benzyl, or R_7 and R_8 together are tetramethylene, pentamethylene or $-(CH_2)_2$-O-$(CH_2)_2$-.

[0016] A preferred sub-group is one in which the diphosphine of formula III is chiral and R_6 is C_1-C_4alkyl, or phenyl or benzyl each having from one to three C_1-C_4alkyl or C_1-C_4alkoxy substituents, A represents identical or different groups $-P(R)_2$ wherein R is branched C_3-C_6alkyl, cyclohexyl, phenyl, benzyl, or phenyl or benzyl each having from one to three C_1-C_4alkyl, C_1-C_4dialkylamino, C_1-C_4alkoxy, $-CF_3$ or partially or completely fluorinated C_1-C_4alkoxy substituents. In the case of those phosphines, chirally substituted compounds wherein R_6 is methyl are especially preferred.

[0017] R in the group $-P(R)_2$ is, within the scope of the preferences mentioned above, especially phenyl or substituted phenyl.

[0018] Most especially preferred among those diphosphine ligands are the following, which may preferably be used in catalysts of formula (I):

{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-phenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-4-N,N-dipropylaminophenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-di-iso-propyl-4-N,N-dimethylaminophenyl)phosphine

{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-di-iso-propyl-4-N,N-dibenzylylaminophenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-4-N,N-dibenzylylaminophenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-4-(1'-pyrrolo)phenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-4-N,N-dipentylaminophenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-4-N,N-dimethylaminophenyl)phosphine
{(R)-1-[(S)-2-di(4-methoxyphenyl)phosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-4-N,N-dimethylaminophenyl)phosphine and especially
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-phenyl)phosphine.

[0019] The preparation of ferrocenyldiphosphine ligands is described, for example, in EP-A-0 564 406 and by T. Hayashi *et al.* in Bull. Chem. Soc. Jpn., 53, pages 1136-1151, and by A. Togni *et al.* in J. Am. Chem. Soc., 116, pages 4062 to 4066 (1994) and in Inorg. Chim. Acta, 222, pages 213 to 224.

[0020] In formulae I and Ia, X is preferably Br and especially I. Also in formulae I and Ia, q is 2 or 3 and r is 1.

[0021] $M^{\oplus}$ in formula Ia may be $(C_1\text{-}C_6\text{alkyl})_4N^{\oplus}$, $Li^{\oplus}$, $Na^{\oplus}$ or $K^{\oplus}$.

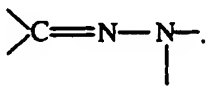
[0022] In an especially preferred form of the process of the invention, the catalysts are those of formula Ib

$$[(DIP)IrI_2H]_2 \quad . \qquad (Ib),$$

wherein DIP is as defined hereinbefore, including the preferred definitions.

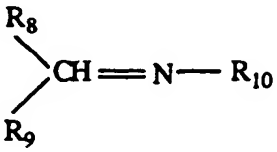
[0023] The iridium catalysts to be used according to the invention may be prepared according to the processes described in US-A-5 112 999.

[0024] Suitable imines are especially those which contain at least one $\rangle C{=}N-$ group. If the groups are substituted asymmetrically and are thus compounds having a prochiral ketimine group, it is possible in the process of the invention for mixtures of optical isomers or pure optical isomers to be formed if enantioselective or diastereoselective iridium catalysts are used. The imines may contain further chiral carbon atoms. The free bonds in the above formulae may be saturated with hydrogen or organic radicals having from 1 to 22 carbon atoms or organic hetero radicals having from 1 to 20 carbon atoms and at least one hetero atom from the group O, S, N and P. The nitrogen atom of the group $\rangle C{=}N-$ may also be saturated with NH_2 or a primary amino group having from 1 to 22 carbon atoms or a secondary amino group having from 2 to 40 carbon atoms. The organic radicals may be substituted, for example, by F, Cl, Br, C_1-C_4haloalkyl, wherein halogen is preferably F or Cl, -CN, $-NO_2$, $-CO_2H$, $-CONH_2$, $-SO_3H$, $-PO_3H_2$, or by C_1-C_{12}alkyl esters, C_1-C_{12}alkyl amides, phenyl esters or benzyl esters of the groups $-CO_2H$, $-SO_3H$ and $-PO_3H_2$. Aldimine and ketimine groups are especially reactive and therefore a selective hydrogenation of $\rangle C{=}N-$ groups in addition to the groups $\rangle C{=}C\langle$ and/or $\rangle C{=}O$ is possible with the process of the invention. Aldimine and ketimine groups are also be understood as including hydrazone groups



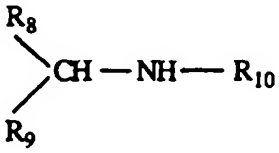
[0025] The process of the invention is suitable especially for the hydrogenation of aldimines, ketimines and hydrazones with the formation of corresponding amines and hydrazines. The ketimines are preferably N-substituted. It is preferable to use chiral iridium catalysts and to hydrogenate enantiomerically pure, chiral or prochiral ketimines to prepare optical isomers, the optical yields (enantiomeric excess, ee) being, for example, higher than 30%, preferably higher than 50%, and it being possible to obtain yields of more than 90%. The optical yield indicates the ratio of the two stereoisomers formed, which ratio may be, for example, greater than 2:1 and preferably greater than 4:1.

[0026] The imines are preferably imines of formula IV



(IV),

which are hydrogenated to form amines of formula V



(V)

wherein

R_{10} is preferably a substituent;
and wherein R_{10} is preferably linear or branched C_1-C_{12}alkyl, cycloalkyl having from 3 to 8 ring carbon atoms; heterocycloalkyl bonded via a carbon atom and having from 3 to 8 ring atoms and 1 or 2 hetero atoms from the group O, S and NR_{11}; a C_7-C_{16}aralkyl bonded via an alkyl carbon atom, or C_1-C_{12}alkyl substituted by said cycloalkyl or heterocycloalkyl or heteroaryl;
or wherein R_{10} is C_6-C_{12}aryl, or C_4-C_{11}heteroaryl bonded via a ring carbon atom and having 1 or 2 hetero atoms in the ring; R_{10} being unsubstituted or substituted by -CN, -NO_2, F, Cl, C_1-C_{12}alkyl, C_1-C_{12}alkoxy, C_1-C_{12}alkylthio, C_1-C_6haloalkyl, -OH, C_6-C_{12}-aryl or -aryloxy or -arylthio, C_7-C_{16}-aralkyl or -aralkoxy or -aralkylthio, secondary amino having from 2 to 24 carbon atoms, -$CONR_{12}R_{13}$ or by -$COOR_{12}$, and the aryl radicals and the aryl groups in aralkyl, aralkoxy and aralkylthio in turn being unsubstituted or substituted by -CN, -NO_2, F, Cl, C_1-C_4-alkyl, -alkoxy, -alkylthio, -OH, -$CONR_{12}R_{13}$ or by -$COOR_{12}$;
R_{12} and R_{13} are each independently of the other hydrogen, C_1-C_{12}alkyl, phenyl or benzyl, or R_{12} and R_{13} together are tetra- or penta-methylene or 3-oxapentylene;
R_{11} has independently the same meaning as given for R_{12};
R_8 and R_9 are each independently of the other a hydrogen atom, C_1-C_{12}alkyl or cycloalkyl having from 3 to 8 ring carbon atoms, each of which is unsubstituted or substituted by -OH, C_1-C_{12}alkoxy, phenoxy, benzyloxy, secondary amino having from 2 to 24 carbon atoms, -$CONR_{12}R_{13}$ or by -$COOR_{12}$; C_6-C_{12}aryl or C_7-C_{16}aralkyl each of which is unsubstituted or substituted as R_{10}, or -$CONR_{12}R_{13}$ or -$COOR_{12}$ wherein R_{12} and R_{13} are as defined hereinbefore; or
R_{10} is as defined hereinbefore and R_8 and R_9 together are alkylene having from 2 to 5 carbon atoms that is optionally interrupted by 1 or 2 -O-, -S- or -NR_6- radicals, and/or unsubstituted or substituted by -O or as indicated above for R_8 and R_9 in the meaning of alkyl, and/or condensed with benzene, pyridine, pyrimidine, furan, thiophene or pyrrole; or
R_9 is as defined hereinbefore and R_8 and R_{10} together are alkylene having from 2 to 5 carbon atoms that is optionally interrupted by 1 or 2 -O-, -S- or -NR_{11}- radicals, and/or unsubstituted or substituted by =O or as indicated above for R_8 and R_9 in the meaning of alkyl, and/or condensed with benzene, pyridine, pyrimidine, furan, thiophene or pyrrole.

[0027] The radicals R_8, R_9 and R_{10} may contain one or more centres of chirality.

[0028] R_8, R_9 and R_{10} may be substituted in any desired positions by identical or different radicals, for example by from 1 to 5, preferably from 1 to 3, substituents.

[0029] Suitable substituents for R_8 and for R_9 and R_{10} are:

C_1-C_{12}-, preferably C_1-C_6- and especially C_1-C_4-alkyl, -alkoxy or -alkylthio, e.g. methyl, ethyl, propyl, n-, iso- and tert-butyl, the isomers of pentyl, hexyl, octyl, nonyl, decyl, undecyl and dodecyl, and corresponding alkoxy and alkylthio radicals;
C_1-C_6-, preferably C_1-C_4-haloalkyl having preferably F and Cl as halogen, e.g. trifluoro- or trichloro-methyl, difluorochloromethyl, fluorodichloromethyl, 1,1-difluoroeth-1-yl, 1,1-dichloroeth-1-yl, 1,1,1-trichloro- or 1,1,1-trifluoroeth-2-yl, pentachloroethyl, pentafluoroethyl, 1,1,1-trifluoro-2,2-dichloroethyl, n-perfluoropropyl, iso-perfluoropropyl, n-perfluorobutyl, fluoro- or chloro-methyl, difluoro- or dichloro-methyl, 1-fluoro- or 1-chloro-eth-2-yl or -eth-1-yl, 1-, 2- or 3-fluoro- or 1-, 2- or 3-chloro-prop-1-yl or -prop-2-yl or -prop-3-yl, 1-fluoro- or 1-chloro-but-1-yl, -but-2-yl, -but-3-yl or -but-4-yl, 2,3-dichloro-prop-1-yl, 1-chloro-2-fluoro-prop-3-yl, 2,3-dichlorobut-1-yl;
C_6-C_{12}-aryl, -aryloxy or -arylthio, in which aryl is preferably naphthyl and especially phenyl, C_7-C_{16}-aralkyl, -aralkoxy and -aralkylthio, in which the aryl radical is preferably naphthyl and especially phenyl and the alkylene radical is linear or branched and contains from 1 to 10, preferably from 1 to 6 and especially from 1 to 3, carbon atoms, for example benzyl, naphthylmethyl, 1- or 2-phenyl-eth-1-yl or -eth-2-yl, 1-, 2- or 3-phenyl-prop-1-yl, -prop-2-yl or -prop-3-yl, with benzyl being especially preferred;

the radicals containing the aryl groups mentioned above may in turn be mono- or polysubstituted, for example by C_1-C_4-alkyl, -alkoxy or -alkylthio, halogen, -OH, -$CONR_{12}R_{13}$ or by -$COOR_{12}$, wherein R_{12} and R_{13} are as defined; examples are methyl, ethyl, n- and iso-propyl, butyl, corresponding alkoxy and alkylthio radicals, F, Cl, Br, dimethyl-, methylethyl- and diethyl-carbamoyl and methoxy-, ethoxy-, phenoxy- and benzyloxycarbonyl;

halogen, preferably F and Cl;

secondary amino having from 2 to 24, preferably from 2 to 12 and especially from 2 to 6, carbon atoms, the secondary amino preferably containing 2 alkyl groups, for example dimethyl-, methylethyl-, diethyl-, methylpropyl-, methyl-n-butyl-, di-n-propyl-, di-n-butyl-, di-n-hexyl-amino;

-$CONR_{12}R_{13}$, wherein R_{12} and R_{13} are each independently of the other C_1-C_{12}-, preferably C_1-C_6-, and especially C_1-C_4-alkyl, or R_{12} and R_{13} together are tetra- or penta-methylene or 3-oxapentylene, the alkyl being linear or branched, e.g. dimethyl-, methylethyl-, diethyl-, methyl-n-propyl-, ethyl-n-propyl-, di-n-propyl-, methyl-n-butyl-, ethyl-n-butyl-, n-propyl-n-butyl- and di-n-butyl-carbamoyl;

-$COOR_{12}$, wherein R_{12} is C_1-C_{12}-, preferably C_1-C_6-alkyl, which may be linear or branched, e.g. methyl, ethyl, n- and iso-propyl, n-, iso- and tert-butyl, and the isomers of pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl.

[0030] R_8, R_9 and R_{10} may contain especially functional groups, such as keto groups, -CN, -NO_2, carbon double bonds, N-O-, aromatic halogen groups and amide groups.

[0031] R_8 and R_9 as heteroaryl are preferably a 5- or 6-membered ring having 1 or 2 identical or different hetero atoms, especially O, S or N, which contains preferably 4 or 5 carbon atoms and can be condensed with benzene. Examples of heteroaromatics from which R_8 and R_9 can be derived are furan, pyrrole, thiophene, pyridine, pyrimidine, indole and quinoline.

[0032] R_8 and R_9 as heteroaryl-substituted alkyl are derived preferably from a 5- or 6-membered ring having 1 or 2 identical or different hetero atoms, especially O, S or N, that contains preferably 4 or 5 carbon atoms and can be condensed with benzene. Examples of hetero-aromatics are furan, pyrrole, thiophene, pyridine, pyrimidine, indole and quinoline.

[0033] R_8 and R_9 as heterocycloalkyl or as heterocycloalkyl-substituted alkyl contain preferably from 4 to 6 ring atoms and 1 or 2 identical or different hetero atoms from the group O, S and NR_{11}. It can be condensed with benzene. It may be derived, for example, from pyrrolidine, tetrahydrofuran, tetrahydrothiophene, indane, pyrazolidine, oxazolidine, piperidine, piperazine or morpholine.

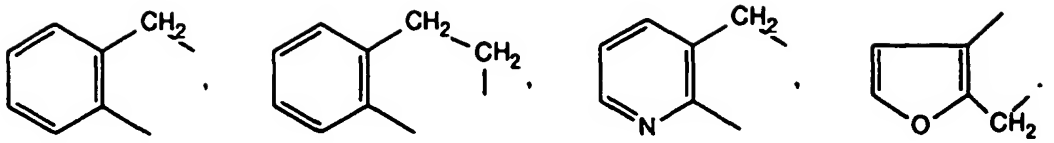
[0034] R_8, R_9 and R_{10} as alkyl are preferably unsubstituted or substituted C_1-C_6-, especially C_1-C_4-alkyl, which may be linear or branched. Examples are methyl, ethyl, iso- and n-propyl, iso-, n- and tert-butyl, the isomers of pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl.

[0035] R_8, R_9 and R_{10} as unsubstituted or substituted cycloalkyl contain preferably from 3 to 6, especially 5 or 6, ring carbon atoms. Examples are cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.

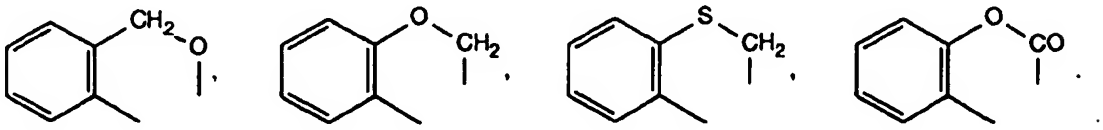
[0036] R_8, R_9 and R_{10} as aryl are preferably unsubstituted or substituted naphthyl and especially phenyl. R_8, R_9 and R_{10} as aralkyl are preferably unsubstituted or substituted phenylalkyl having from 1 to 10, preferably from 1 to 6 and especially from 1 to 4, carbon atoms in the alkylene, the alkylene being linear or branched. Examples are especially benzyl, and 1-phenyleth-1-yl, 2-phenyleth-1-yl, 1-phenylprop-1-yl, 1-phenylprop-2-yl, 1-phenylprop-3-yl, 2-phenylprop-1-yl, 2-phenylprop-2-yl and 1-phenylbut-4-yl.

[0037] In R_9 and R_{10} as -$CONR_{12}R_{13}$ and -$COOR_{12}$, R_{12} and R_{13} are preferably C_1-C_6-, especially C_1-C_4-alkyl, or R_{12} and R_{13} together are tetramethylene, pentamethylene or 3-oxapentylene. Examples of alkyl are mentioned hereinbefore.

[0038] R_8 and R_9 together or R_8 and R_{10} together as alkylene are preferably interrupted by 1 -O-, -S- or -NR_{11}-, preferably -O-. R_8 and R_9 together or R_8 and R_{10} together form, with the carbon atom or with the -N=C group to which they are respectively bonded preferably a 5-or 6-membered ring. For the substituents the preferences mentioned hereinbefore apply. As condensed alkylene, R_8 and R_9 together or R_8 and R_{10} together are preferably alkylene condensed with benzene or pyridine. Examples of alkylene are: ethylene, 1,2- or 1,3-propylene, 1,2-, 1,3- or 1,4-butylene, 1,5-pentylene and 1,6-hexylene. Examples of interrupted or =O-substituted alkylene are 2-oxa-1,3-propylene, 2-oxa-1,4-butylene, 2-oxa- or 3-oxa-1,5-pentylene, 3-thia-1,5-pentylene, 2-thia-1,4-butylene, 2-thia-1,3-propylene, 2-methylimino-1,3-propylene, 2-ethylimino-1,4-butylene, 2- or 3-methylimino-1,5-pentylene, 1-oxo-2-oxa-1,3-propylene, 1-oxo-2-oxa-1,4-butylene, 2-oxo-3-oxa-1,4-butylene and 1-oxa-2-oxo-1,5-pentylene. Examples of condensed alkylene are:



[0039] Examples of condensed and interrupted and unsubstituted or =O-substituted alkylene are:

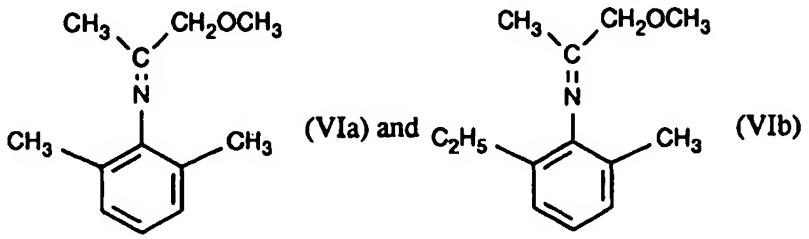


R_{12} and R_{13} are preferably each independently of the other hydrogen, C_1-C_4alkyl, phenyl or benzyl. R_{11} is preferably hydrogen or C_1-C_4alkyl.

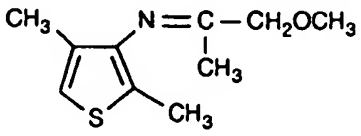
[0040] A further preferred group is formed by prochiral imines in which in formula IV R_8 and R_9 are different from each other.

[0041] In an especially preferred group, in formula IV R_{10} is 2,6-di-C_1-C_4alkylphen-1-yl and especially 2,6-dimethylphen-1-yl or 2-methyl-6-ethylphen-1-yl, R_8 is C_1-C_4alkyl and especially ethyl or methyl, and R_9 is C_1-C_4alkyl, C_1-C_4alkoxymethyl or C_1-C_4alkoxyethyl, and especially methoxymethyl.

[0042] Of those compounds, imines of formulae



are especially important, as is the imine of formula



[0043] Imines of formula IV are known or they can be prepared in accordance with known processes from aldehydes or ketones and primary amines.

[0044] The molar ratio of imine to iridium catalyst may be, for example, from 1 000 000 to 10, especially from 500 000 to 20, more preferably from 200 000 to 100 and most preferably from 100 000 to 100.

[0045] The process is carried out preferably at a temperature of from -20 to 100°C, especially from 0 to 80°C and more especially from 10 to 70°C, and preferably at a hydrogen pressure of from 2×10^5 to 1.5×10^7 Pa (5 to 150 bar), especially from 10^6 to 10^7 Pa (10 to 100 bar).

[0046] The reaction can be carried out in the absence or in the presence of solvents. Suitable solvents, which can

be used alone or as a mixture of solvents, are, for example:
aliphatic and aromatic hydrocarbons, such as pentane, hexane, cyclohexane, methylcyclohexane, benzene, toluene and xylene; ethers, such as diethyl ether, diethylene glycol dimethyl ether, tetrahydrofuran and dioxane; halogenated hydrocarbons, such as methylene chloride, chloroform, 1,1,2,2-tetrachloroethane and chlorobenzene; esters and lactones, such as ethyl acetate, butyrolactone and valerolactone; acid amides and lactams, such as dimethylformamide, dimethylacetamide and N-methylpyrrolidone, and ketones, such as acetone, dibutyl ketone, methyl isobutyl ketone and methoxyacetone.

[0047] In detail, the process according to the invention can be carried out by first dissolving the catalyst in a solvent or in a portion of the substance to be hydrogenated and then adding the imine (where appropriate as a solution). That mixture is hydrogenated in an autoclave and the reaction mixture is isolated and purified in a manner known *per se,* for example by precipitation, extraction or distillation. The catalyst may be formed *in situ* in the starting phase of the hydrogenation.

[0048] Before the hydrogenation reaction, a protective gas atmosphere is advantageously used. It is advantageous to ensure that the catalyst solution stands for only a short time, and to carry out the hydrogenation of the imines as soon as possible after the preparation of the catalyst solution.

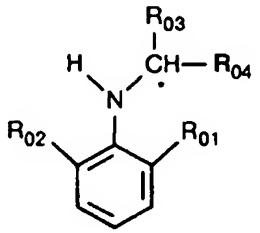
[0049] In the case of the hydrogenation of aldimines and ketimines, the aldimines and ketimines can also be formed *in situ* before or during the hydrogenation. In a preferred form, an amine and an aldehyde or a ketone are mixed together and added to the catalyst solution and the aldimine or ketimine formed *in situ* is hydrogenated. It is also possible, however, to use an amine, a ketone or an aldehyde together with the catalyst as the initial batch and to add the ketone or the aldehyde or the amine thereto, either all at once or in metered amounts.

[0050] The hydrogenation can be carried out continuously or batchwise in various types of reactor. Preference is given to those reactors which allow comparatively good intermixing and good removal of heat, such as, for example, loop reactors. That type of reactor has proved to be especially satisfactory when small amounts of catalyst are used.

[0051] The process according to the invention yields the corresponding amines in short reaction times while having chemically a high degree of conversion, with surprisingly excellent optical yields (ee) of 70 % or more being obtained even at relatively high temperatures of more than 50°C, and even with high molar ratios of imine to catalyst.

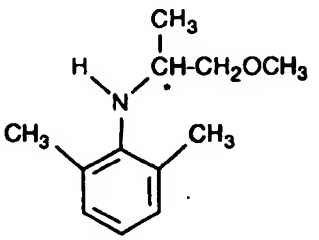
[0052] The hydrogenated organic compounds that can be prepared in accordance with the invention, for example the amines, are biologically active substances or are intermediates for the preparation of such substances, especially in the field of the preparation of pharmaceuticals and agrochemicals. For example, o,o-dialkylarylketamine derivatives, especially those having alkyl and/or alkoxyalkyl groups, are effective as fungicides, especially as herbicides. The derivatives may be amine salts, acid amides, for example of chloroacetic acid, tertiary amines and ammonium salts (see, for example, EP-A-0 077 755 and EP-A-0 115 470).

[0053] Especially important in this connection are the optically active amines of formula VII

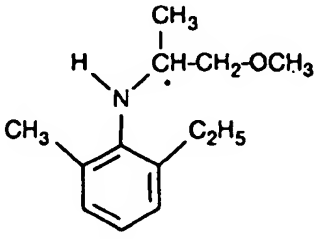


(VII),

which can be prepared using the processes according to the invention from the imines of formula (VI) in the presence of asymmetric iridium catalysts, and wherein R_{01}, R_{02} and R_{03} are each independently of the others C_1-C_4alkyl, and R_{04} is C_1-C_4alkyl or C_1-C_4-alkoxymethyl or C_1-C_4alkoxyethyl, and especially the amines of the formulae



(VIIa) and



(VIIb)

which can be prepared from the imines of formulae (VIa) and (VIb) and can be converted in accordance with methods that are customary *per se* with chloroacetic acid into the desired herbicides of the chloroacetanilide type; of those compounds, the compounds having the S-configuration at the asymmetric C* atom are most especially preferred.

[0054] The Examples that follow illustrate the invention in more detail. The chemical conversion is determined by gas chromatography (column 2m OV 101 / 100 to 200°C at 10°C/min). The optical yields (enantiomeric excess, ee) are determined either by gas chromatography [Chirasil-Val column, 50 m, manufacturer: Alltech, USA, T = 150°C, isothermic], by HPLC (Chiracel OD column) or by ^{1}H-NMR spectroscopy (using shift reagents).

[0055] For the diphosphines, the following abbreviations are used:

{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-bis[(3,5-dimethyl)phenyl]phosphine [PPF-P(xyl)$_2$]

{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-bis[(3,5-dimethyl-4-dimethylamino)phenyl]phosphine [PPF-P(NMe_2xyl)$_2$]

{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di-(tertiary butyl)phosphine [PPF-P(t-Bu)$_2$]

A) Preparation of starting compounds and catalysts

Example A1: Preparation of [(PPF-P(xyl)$_2$)Ir(cyclooctadiene)]BF_4 (A1)

[0056] 320 mg (1.64 mmol) of $AgBF_4$ are added to a solution of 525 mg (0.78 mmol) of [Ir(cydooxctadiene)Cl]$_2$ in 10 ml of methylene chloride and stirred. After 15 minutes, 1 g (1.57 mmol) of PPF-P(xyl)$_2$ in 10 ml of methylene chloride is slowly added dropwise. The deep-red solution formed is stirred at room temperature for 12 h with the exclusion of light. It is then filtered over Celite and the solvent is evaporated off *in vacuo* to yield 1.54 g (96%) of a deep-red solid (A1).
$^{31}P\{^1H\}$-NMR (121 MHz; $CDCl_3$)
40.34 and 8.68 (AX; $^2J_{PP}$ = 21.9 and 23.6 Hz; 92%); 6.49 and 25.11 (AX; $^2J_{PP}$ = 23.96 and 23.63 Hz; 6%); 18.87 (s; 2%).

Example A2: Preparation of [(PPF-P(NMe_2xyl)$_2$)Ir(cyclooctadiene)]BF_4 (A2)

[0057] Preparation is effected analogously to Example A1. The isolated product contains, according to the NMR spectrum, approximately 10% by-products.
$^{31}P\{^1H\}$-NMR (121 MHz; $CDCl_3$)
39.76 and 10.24 (AX; $^2J_{PP}$ = 21.5 and 21.0 Hz)

Example A3: Preparation of [(PPF-P(t-Bu)$_2$)Ir(cyclooctadiene)]BF_4 (A3)

[0058] Preparation is effected analogously to Example A1. The isolated product contains, according to the NMR spectrum, approximately 10% by-products.
$^{31}P\{^1H\}$-NMR (121 MHz; $CDCl_3$).
61.38 and 9.52 (AX; $^2J_{PP}$ = 10.5 and 17.7 Hz)

Example A4: Preparation of [(PPF-P(xyl)$_2$)IrH_2]$_2$ (Ir1)

[0059]

a) 6.5 g (48.6 mmol) of LiI are added to a solution of 1.5 mmol of compound A1 in 20 ml of acetone and the mixture is then refluxed with stirring for 5 h. After cooling, the solvent is removed using a rotary evaporator. The orange-red residue is dissolved in 100 ml of methylene chloride, left to stand at room temperature for 12 h, and the white precipitate which forms is removed by filtration. The filtrate is washed twice with 100 ml of water and the solvent is then removed using a rotary evaporator. The orange-brown residue is taken up in 20 ml of methylene chloride, 50 ml of pentane are added thereto and the orange-brown precipitate is removed by filtration. The filtrate is again concentrated to dryness, taken up in 5 ml of methylene chloride, 20 ml of pentane are added thereto and the red-brown precipitate is removed by filtration. The last procedure is repeated, and the three precipitates are combined, washed with 10 ml of water, twice with 10 ml of ethanol, twice with 5 ml of diethyl ether and three times with 10 ml of pentane. 1.35 g (83%) of an orange-brown solid are obtained as a mixture of isomers.
^{1}H-NMR (300 MHz; $CDCl_3$)
Hydride region:
Main isomer -17.25 (dd, ΣJ = 25.5 Hz, 73%)

Other resonances: -16.15 (m, broad, 5%); -16.22 (dd, ΣJ = 24.6 Hz, 6%); -19.16 (t, ^2J_P = 16.1 Hz, 6%); -19.72 (t, ^2J_P = 16.1 Hz, 5%); 20.86 (dd, ΣJ = 28.9 Hz, 5%) ppm.

b) 450 mg (0.44 mmol) of compound A1 and 1.5 g of LiI (26 equivalents) are mixed with 10 ml of acetone, the mixture is refluxed for 2 h and then the solvent is removed to yield a deep-red solid comprising 2 position isomers as the main products, which are separated as follows:

First the residue is dried under a high vacuum for 12 h, then 20 ml of methylene chloride are added, the insoluble constituents are removed by filtration and the solvent is removed *in vacuo*. That procedure is repeated three times. Then 5 ml of toluene are added and the yellow-orange solution is decanted from the dark red oil which has separated. The procedure is repeated twice. The three filtrates are combined and concentrated to dryness by evaporation. 5 ml of toluene are added, the yellow solution is decanted from the red oil and the procedure is repeated. The filtrates and oil fractions are combined. 30 ml of pentane are added to the yellow toluene solution (10 ml) and the yellow solid which precipitates is removed by filtration. The filtrate is concentrated by evaporation, dissolved with 4 ml of toluene, 30 ml of pentane are added and the yellow solid which precipitates is then removed by filtration. The filtrate is concentrated by evaporation and the brown solid is washed twice with 2 ml of ethanol and twice with 2 ml of diethyl ether. After drying, 65 mg (14%) of compound Ir2 are obtained in the form of a fawn-coloured solid.

^{1}H-NMR (300 MHz; $CDCl_3$)

Hydride region:

Main isomer -17.22 (dd, ΣJ = 25.6 Hz, 92%)

$^{31}P\{^1H\}$-NMR (121 MHz; $CDCl_3$).

Main isomer 10.4 and -22.2 (AX; $^2J_{PP}$ = 18.5 and 15.8 Hz, 92%).

[0060] The red oil is dried *in vacuo* and dissolved in methylene chloride, and undissolved portions are removed by filtration. The solvent is then evaporated off and the procedure is repeated twice. 270 mg (57%) of compound Ir3 are obtained in the form of a reddish brown solid.

^{1}H-NMR (300 MHz; $CDCl_3$)

Hydride region:

Main isomer -19.74 (t, $^2J_{HP}$ = 16.3 Hz, 84%)

$^{31}P\{^1H\}$-NMR (121 MHz; $CDCl_3$).

Main isomer 15.5 and -8.6 (AX; $^2J_{PP}$ = 12.5 and 12.8 Hz, 84%).

Example A5: Preparation of $[(PPF\text{-}P(NMe_2xyl)_2)IrHI_2]_2$ (Ir4)

[0061] 1.4 g (39 equivalents) of LiI are added to a solution of 0.134 mmol of compound A2 in 8 ml of acetone and the mixture is refluxed with stirring for 5 h. It is then concentrated using a rotary evaporator to a volume of 4 ml and the yellow-orange solid residue is separated off by centrifuging. The solid is washed twice with 2 ml of acetone, with 2 ml of methylene chloride, with 2 ml of chloroform and twice with 5 ml of pentane. After drying *in vacuo*, 125 mg (40%) of a yellow-orange solid are obtained.

^{1}H-NMR (300 MHz; CD_3CN)

Hydride region: -20.51 (t, $^2J_{HP}$ = -16.1 Hz, 87%); -20.28 t, $^2J_{HP}$ = -17.0 Hz, 13%).

$^{31}P\{^1H\}$-NMR (121 MHz; CD_3CN)

11.8 and -14.4 (s, 85%); 8.1 and -16.4 (m, 15%).

Example A6: Preparation of $[(PPF\text{-}P(t\text{-}Bu)_2)IrHI_2]_2$ (Ir5)

[0062] 2.6 g of LiI (19.43 mmol) are added to a solution of 0.245 mmol of compound A3 in 15 ml of acetone and the mixture is then refluxed with stirring for 8 h. The solvent is then removed using a rotary evaporator and the dark red solid residue is dried under a high vacuum. The solid is dissolved in 20 ml of methylene chloride and the insoluble constituents are removed by filtration. That procedure is repeated twice. The residue is again taken up in methylene chloride and washed twice with 10 ml of water. The methylene chloride is then removed using a rotary evaporator and the reddish brown residue is washed three times with 10 ml of ethanol and three times with 10 ml of diethyl ether. After drying *in vacuo*, 450 mg (93%) of a reddish brown solid are obtained.

^{1}H-NMR (300 MHz; $CDCl_3$)

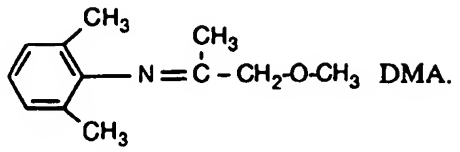
Hydride region: -18.88 (dd, Σ^2J_{HP} = 32 Hz, 40%); -21.48 (t, $^2J_{HP}$ = 15.5 Hz, 60%).

$^{31}P\{^1H\}$-NMR (121 MHz; $CDCl_3$)

60.4 and 8.0 (s, broad, 40%); 54.8 and -9.9 (s, broad, 60%).

B) Hydrogenation of imines

[0063] The following abbreviations are used for the imines used:



DMA.

Examples B1-B13:

[0064] In a 50 ml steel autoclave, the catalyst (0.0157 mmol) is dissolved in 2.5 ml of methylene chloride and 7.5 ml of tetrahydrofuran. The imine (7.83 mmol, 500 equivalents) is added to the solution. The autoclave is degassed three times with hydrogen at 25 bar. The reaction mixture is then heated to 30°C and hydrogen is passed in under pressure. To examine the course of the reaction, samples may be taken periodically *via* a built-in cannula. t_{Con} is the time taken before the conversion indicated is reached and t_{End} is the total reaction time. S/Ir is the molar ratio of DMA to iridium catalyst. Ir denotes the iridium catalysts Ir1 to Ir5 according to Examples A4 to A6. In Examples B3 and B10 tetrahydrofuran is used, in Example B4 methylene chloride, in Example B5 toluene, and in Example B6 methyl tert-butyl ether. The results are given in Table 1.

Table 1

Ir	S/Ir	H_2 pressure (bar)	t_{Con} (% conversion)	t_{End}	Yield (%)	Optical Yield (% ee)	Example
Ir1	500	40	15'(82)	25'	98	82(S)	B1
Ir1	500	10	30'(51)	1h15	98	82(S)	B2
Ir1	500	10	30'(61)	1h	98	81(S)	B3
Ir1	500	10	1h (40)	3h25	80	77(S)	B4
Ir1	500	10	2h (49)	3h05	82	80(S)	B5
Ir1	500	40	30'(87)	45'	99	86(S)	B6
Ir2	500	40	15'(91)	45'	100	82(S)	B7
Ir2	500	10	15'(51)	30'	93	82(S)	B8
Ir2	10 000	40	2h (43)	4h	95	82(S)	B9
Ir2	85 000	40	24h(26)	96h	95	82(S)	B10
Ir3	500	40	15'(47)	30'	96	82(S)	B11
Ir4	500	40	15'(68)	25'	98	83(S)	B12
Ir5	500	40	24h(14)	95h	31	42(S)	B13

Claims

1. A process for the preparation of primary or secondary amines by hydrogenation of imines with hydrogen at elevated pressure and in the presence of a dinuclear Ir(III) complex having ditertiary diphosphine ligands, halide bridges, halide and hydride ligands, or an Ir(III) halide complex salt containing ditertiary diphosphine ligands, as catalyst, wherein the catalyst corresponds to formula I or Ia or to mixtures of at least two compounds of formula I, at least two compounds of formulae I and Ia, or at least two compounds of formula Ia

$$[(DIP)IrX_qY_r]_2 \quad (I),$$

$$[(DIP)X_4]^{\ominus}Me^{\oplus} \quad (Ia),$$

wherein

DIP is the ditertiary diphosphine ligand of a ferrocenyldiphosphine the phosphine groups of which are either bonded directly or *via* a bridge group $-CR_vR_w-$ in the ortho positions of a cyclopentadienyl ring or are each bonded to a cyclopentadienyl ring of a ferrocenyl, so that a 5-, 6- or 7-membered ring is formed together with the Ir atom;
R_v and R_w are each independently of the other hydrogen, C_1-C_8alkyl, C_1-C_4fluoroalkyl, phenyl or benzyl, or are phenyl or benzyl each having from 1 to 3 C_1-C_4alkyl or C_1-C_4-alkoxy substituents;
X is Cl, Br or I;
Y is H;
q is a number 2 or 3 and r is 0 or 1, the sum of q+r being equal to 3; and
$Me^{\oplus}$ is an alkali metal cation or quaternary ammonium.

2. A process according to claim 1, wherein R_w is hydrogen.

3. A process according to claims 1 and 2, wherein R_v is C_1-C_4alkyl.

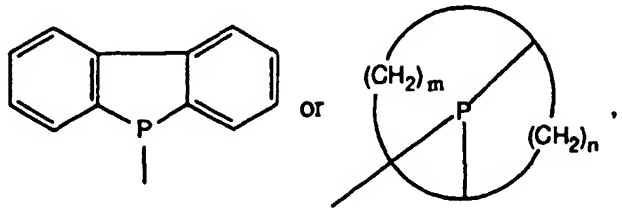
4. A process according to claim 3, wherein R_v is methyl.

5. A process according to claim 1, wherein the ditertiary diphosphine contains at least one chiral group and is a stereoisomer or a pair of diastereoisomers.

6. A process according to claim 1, wherein the phosphine groups contain two identical or different unsubstituted or substituted hydrocarbon radicals having from 1 to 20 carbon atoms.

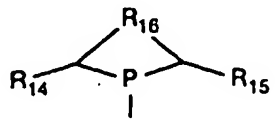
7. A process according to claim 1, wherein the diphosphines contain two identical or different radicals from the following group: linear or branched C_1-C_{12}alkyl; unsubstituted or C_1-C_6alkyl- or C_1-C_6alkoxy-substituted C_5-C_{12}cycloalkyl, C_5-C_{12}cycloalkyl-CH_2-, phenyl and benzyl; and phenyl and benzyl each substituted by halogen, C_1-C_6haloalkyl, $(C_1$-$C_{12}alkyl)_3Si$, $(C_5H_5)_3Si$, C_1-C_6haloalkoxy, $-NH_2$, $phenyl_2N$-, $benzyl_2N$-, morpholinyl, piperidinyl, pyrrolidinyl, $(C_1$-$C_{12}alkyl)_2N$-, -ammonium-$X_1^{\ominus}$-, $-SO_3M_1$, $-CO_2M_1$, $-PO_3M_1$ or by -COO-C_1-C_6alkyl; wherein M_1 is an alkali metal or hydrogen and $X_1^{\ominus}$ is the anion of a monobasic acid, and M_1 is preferably H, Li, Na or K.

8. A process according to claim 1, wherein
the phosphine groups are radicals of the formula



wherein m and n are each independently of the other an integer from 2 to 10 and the sum of m+n is equal to from 4 to 12.

9. A process according to claim 1, wherein the phosphine groups are radicals of the formula



wherein R_{16} is C_1-C_4alkylene, preferably C_2- or C_3-alkylene, and R_{14} and R_{15} are each independently of the other hydrogen, C_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6haloalkyl, C_5- or C_6-cycloalkyl, or phenyl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or by halogen, or benzyl that is unsubstituted or substituted by

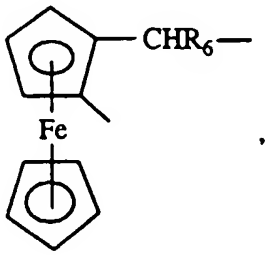
C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or by halogen.

10. A process according to claim 1, wherein the ferrocenyldiphosphine corresponds to formula II

$$R_1R_2P\text{-}R_5\text{-}PR_3R_4 \qquad \text{(II)},$$

wherein

R_1, R_2, R_3 and R_4 are each independently of the others a hydrocarbon radical having from 1 to 20 carbon atoms that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6alkoxy, halogen, C_1-C_6haloalkyl, $(C_1$-C_{12}alkyl$)_3Si$, $(C_6H_5)_3Si$, C_1-C_6haloalkoxy, $-NH_2$, phenyl$_2$N-, benzyl$_2$N-, morpholinyl, piperidinyl, pyrrolidinyl, $(C_1$-C_{12}alkyl$)_2$N-, -ammonium-$X_1^{\ominus}$, $-SO_3M_1$, $-CO_2M_1$, $-PO_3M_1$ or by -COO-C_1-C_6alkyl, wherein M_1 is an alkali metal or hydrogen and $X_1^{\ominus}$ is the anion of a monobasic acid;
R_1 and R_2 together and R_3 and R_4 together form a C_1-C_4alkylene radical that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6haloalkyl, C_5- or C_6-cycloalkyl, by phenyl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or by halogen, or by benzyl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or by halogen; and
R_5 is a radical of the formula



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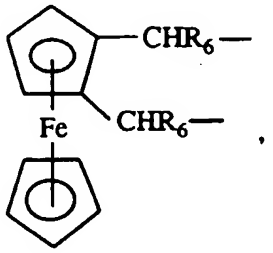

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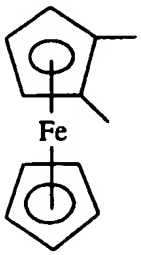

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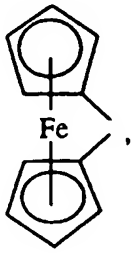

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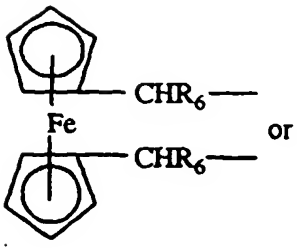

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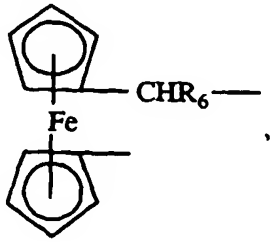
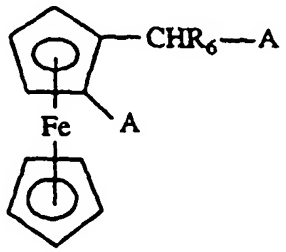


,

wherein R_6 is hydrogen, C_1-C_8alkyl, C_1-C_4fluoroalkyl, phenyl or phenyl having from 1 to 3 C_1-C_4alkyl or C_1-C_4alkoxy substituents.

11. A process according to claim 10, wherein R_1, R_2, R_3 and R_4 are identical or different radicals from the following group: C_1-C_6alkyl; cyclopentyl and cyclohexyl that are unsubstituted or have from one to three C_1-C_4alkyl or C_1-C_4alkoxy substituents; and benzyl and especially phenyl that are unsubstituted or have from one to three C_1-C_4alkyl, C_1-C_4alkoxy, F, Cl, C_1-C_4fluoroalkyl or C_1-C_4fluoroalkoxy substituents.

12. A process according to claim 10, wherein the disphosphine ligands DIP are those of formula III



(III).

wherein

R_6 is hydrogen and especially methyl; and
A represents identical or different groups -$P(R)_2$ wherein R is C_1-C_6alkyl, cyclohexyl, phenyl, benzyl, or phenyl or benzyl each having from one to three C_1-C_4alkyl, disubstituted amino, C_1-C_4alkoxy, -CF_3 or partially or completely fluorinated C_1-C_4alkoxy substituents.

13. A process according to claim 12, wherein the diphosphine of formula III is chiral and R_6 is C_1-C_4alkyl, or phenyl or benzyl each having from one to three C_1-C_4alkyl or C_1-C_4-alkoxy substituents, A represents identical or different groups -$P(R)_2$ wherein R is branched C_3-C_6alkyl, cyclohexyl, phenyl, benzyl, or phenyl or benzyl each having from one to three C_1-C_4alkyl, C_1-C_4dialkylamino, C_1-C_4alkoxy, -CF_3 or partially or completely fluorinated C_1-C_4alkoxy substituents.

14. A process according to claim 13, wherein R in the group $P(R)_2$ is phenyl or substituted phenyl.

15. A process according to claim 1, wherein the diphosphines are selected from the following group:

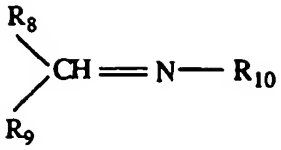
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-phenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-4-N,N-dipropylaminophenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-di-iso-propyl-4-N,N-dimethylaminophenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-di-iso-propyl-4-N,N-dibenzylylaminophenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-4-N,N-dibenzylylaminophenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-4-(1'-pyrrolo)phenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-4-N,N-dipentylaminophenyl)phosphine
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-4-N,N-dimethylaminophenyl)phosphine
{(R)-1-[(S)-2-di(4-methoxyphenyl)phosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-4-N,N-dimethylaminophenyl)phosphine and especially
{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-phenyl)phosphine.

16. A process according to claim 1, wherein the catalysts are those of formula Ib

$$[(DIP)IrI_2H]_2 \qquad (Ib)$$

wherein DIP is as defined in claim 1.

17. A process according to claim 1, wherein the imines are imines of formula IV



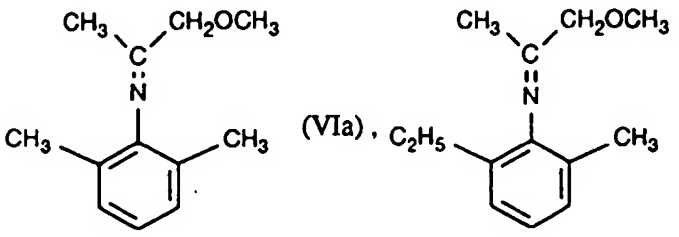
(IV),

wherein R_{10} is linear or branched C_1-C_{12}alkyl, cycloalkyl having from 3 to 8 ring carbon atoms; heterocycloalkyl bonded via a carbon atom and having from 3 to 8 ring atoms and 1 or 2 hetero atoms from the group O, S and NR_{11}; a C_7-C_{16}aralkyl bonded *via* an alkyl carbon atom, or C_1-C_{12}alkyl substituted by said cycloalkyl or heterocycloalkyl or heteroaryl;
or wherein R_{10} is C_6-C_{12}aryl, or C_4-C_{11}heteroaryl bonded *via* a ring carbon atom and having 1 or 2 hetero atoms in the ring; R_{10} being unsubstituted or substituted by -CN, -NO_2, F, Cl, C_1-C_{12}alkyl, C_1-C_{12}alkoxy, C_1-C_{12}alkylthio, C_1-C_6haloalkyl, -OH, C_6-C_{12}-aryl or -aryloxy or -arylthio, C_7-C_{16}-aralkyl or -aralkoxy or -aralkylthio, secondary amino having from 2 to 24 carbon atoms, -$CONR_{12}R_{13}$ or by -$COOR_{12}$, and the aryl radicals and the aryl groups in aralkyl, aralkoxy and aralkylthio in turn being unsubstituted or substituted by -CN, -NO_2, F, Cl, C_1-C_4-alkyl, -alkoxy, -alkylthio, -OH, -$CONR_{12}R_{13}$ or by -$COOR_{12}$;
R_{12} and R_{13} are each independently of the other hydrogen, C_1-C_{12}alkyl, phenyl or benzyl, or R_{12} and R_{13} together are tetra- or penta-methylene or 3-oxapentylene;
R_{11} has independently the same meaning as given for R_{12};
R_8 and R_9 are each independently of the other a hydrogen atom, C_1-C_{12}alkyl or cycloalkyl having from 3 to 8 ring carbon atoms, each of which is unsubstituted or substituted by -OH, C_1-C_{12}alkoxy, phenoxy, benzyloxy, secondary amino having from 2 to 24 carbon atoms, -$CONR_{12}R_{13}$ or by -$COOR_{12}$; C_6-C_{12}aryl or C_7-C_{16}aralkyl each of which is unsubstituted or substituted as R_{10}, or -$CONR_{12}R_{13}$ or -$COOR_{12}$ wherein R_{12} and R_{13} are as defined hereinbefore; or
R_{10} is as defined hereinbefore and R_8 and R_9 together are alkylene having from 2 to 5 carbon atoms that is optionally interrupted by 1 or 2 -O-, -S- or -NR_6- radicals, and/or unsubstituted or substituted by =O or as indicated above for R_8 and R_9 in the meaning of alkyl, and/or condensed with benzene, pyridine, pyrimidine, furan, thiophene or pyrrole; or
R_9 is as defined hereinbefore and R_8 and R_{10} together are alkylene having from 2 to 5 carbon atoms that is optionally interrupted by 1 or 2 -O-, -S- or -NR_{11}- radicals, and/or unsubstituted or substituted by =O or as indicated above for R_8 and R_9 in the meaning of alkyl, and/or condensed with benzene, pyridine, pyrimidine, furan, thiophene or pyrrole.

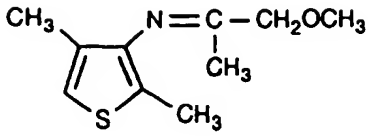
18. A process according to claim 17, wherein R_8 and R_9 are different from each other.

19. A process according to claim 17, wherein, in formula IV, R_{10} is 2,6-di-C_1-C_4alkylphen-1-yl, R_8 is C_1-C_4alkyl, and R_9 is C_1-C_4alkyl, C_1-C_4alkoxymethyl or C_1-C_4alkoxyethyl.

20. A process according to claim 17, wherein the imines are imines of the formulae



(VIa), (VIb),



(VIc).

21. A process according to claim 1, wherein the molar ratio of imine to iridium catalyst is from 1 000 000 to 10.

22. A process according to claim 21, wherein the molar ratio of imine to iridium catalyst is from 500 000 to 20.

23. A process according to claim 21, wherein the molar ratio of imine to iridium catalyst is from 200 000 to 100.

24. A process according to claim 21, wherein the molar ratio of imine to iridium catalyst is from 100 000 to 100.

25. A process according to claim 1, wherein the reaction temperature is from -20 to 100°C.

26. A process according to claim 1, wherein the hydrogen pressure is from 2×10^5 to 1.5×10^7 Pa.

27. A process according to claim 1, wherein the reaction is carried out in the presence of a solvent.

Patentansprüche

1. Verfahren zur Herstellung von primären oder sekundären Aminen durch Hydrierung von Iminen mit Wasserstoff bei erhöhtem Druck und in Gegenwart eines zweikernigen Ir(III)-Komplexes mit ditertiären Diphosphinliganden, Halogenidbrükken, Halogenid- und Hydridliganden oder eines ditertiäre Diphosphinliganden-enthaltenden Ir(III)-Halogenidkomplexsalzes als Katalysator, wobei der Katalysator der Formel I oder Ia oder Gemischen von mindestens zwei Verbindungen der Formel I, mindestens zwei Verbindungen der Formeln I und Ia oder mindestens zwei Verbindungen der Formel Ia entspricht

$$[(DIP)IrX_qY_r]_2 \qquad (I),$$

$$[(DIP)X_4]^-Me^{\oplus} \qquad (Ia),$$

worin

DIP den ditertiären Diphosphinliganden eines Ferrocenyldiphosphins darstellt, dessen Phosphingruppen entweder direkt oder über eine Brückengruppe $-CR_vR_w-$ in den ortho-Stellungen eines Cyclopentadienylrings gebunden sind oder jeder an einen Cyclopentadienylring eines Ferrocenyls gebunden ist, so daß ein 5-, 6- oder 7-gliedriger Ring, zusammen mit dem Ir-Atom, gebildet wird;
R_v und R_w jeweils unabhängig voneinander Wasserstoff, C_1-C_8-Alkyl, C_1-C_4-Fluoralkyl, Phenyl oder Benzyl bedeuten, oder Phenyl oder Benzyl mit 1 bis 3 C_1-C_4-Alkyl- oder C_1-C_4-Alkoxysubstituenten bedeuten;
X Cl, Br oder I darstellt;
Y H darstellt;
q eine Zahl 2 oder 3 ist und r 0 oder 1 ist, wobei die Summe von q+r gleich 3 ist; und
$Me^{\oplus}$ ein Alkalimetallkation oder quaternäres Ammonium darstellt.

2. Verfahren nach Anspruch 1, wobei R_w Wasserstoff darstellt.

3. Verfahren nach Ansprüchen 1 und 2, wobei R_v C_1-C_4-Alkyl darstellt.

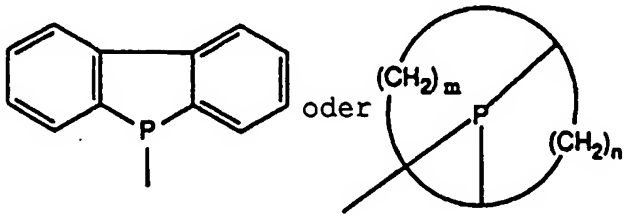
4. Verfahren nach Anspruch 3, wobei R_v Methyl darstellt.

5. Verfahren nach Anspruch 1, wobei das ditertiäre Diphosphin mindestens eine chirale Gruppe enthält und ein Stereoisomer oder ein Diastereoisomerenpaar darstellt.

6. Verfahren nach Anspruch 1, wobei die Phosphingruppen zwei gleiche oder verschiedene unsubstituierte oder substituierte Kohlenwasserstoffreste mit 1 bis 20 Kohlenstoffatomen enthalten.

7. Verfahren nach Anspruch 1, wobei die Diphosphine zwei gleiche oder verschiedene Reste der nachstehenden Gruppe enthalten: lineares oder verzweigtes C_1-C_{12}-Alkyl; unsubstituiertes oder C_1-C_6-Alkyl- oder C_1-C_6-Alkoxy-substituiertes C_5-C_{12}-Cycloalkyl, C_5-C_{12}-Cycloalkyl-CH_2-, Phenyl und Benzyl; und jeweils mit Halogen, C_1-C_6-Halogenalkyl, $(C_1$-C_{12}-Alkyl$)_3Si$, $(C_6H_5)_3Si$, C_1-C_6-Halogenalkoxy, $-NH_2$, Phenyl$_2$N-, Benzyl$_2$N-, Morpholinyl, Piperidinyl, Pyrrolidinyl, $(C_1$-C_{12}-Alkyl$)_2$N-, -Ammonium-X_1^-, $-SO_3M_1$, $-CO_2M_1$, $-PO_3M_1$, oder mit $-COO$-C_1-C_6-Alkyl substituiertes Phenyl und Benzyl, wobei M_1 ein Alkalimetall oder Wasserstoff darstellt und X_1^- das Anion einer einbasigen Säure darstellt und M1 vorzugsweise H, Li, Na oder K darstellt.

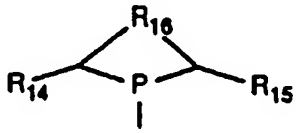
8. Verfahren nach Anspruch 1, wobei die Phosphingruppen Reste der Formel



darstellen,

worin m und n jeweils unabhängig voneinander eine ganze Zahl von 2 bis 10 sind und die Summe von m+n gleich 4 bis 12 ist.

9. Verfahren nach Anspruch 1, wobei die Phosphingruppen Reste der Formel



darstellen,

worin

R_{16} C_1-C_4-Alkylen, vorzugsweise C_2- oder C_3-Alkylen, darstellt, und R_{14} und R_{15} jeweils unabhängig voneinander Wasserstoff, C_1-C_6-Alkyl, C_1-C_6-Alkoxy, C_1-C_6-Halogenalkyl, C_5-oder C_6-Cycloalkyl oder unsubstituiertes oder mit C_1-C_4-Alkyl, C_1-C_4-Alkoxy, C_1-C_4-Halogenalkyl oder mit Halogen substituiertes Phenyl oder unsubstituiertes oder mit C_1-C_4-Alkyl, C_1-C_4-Alkoxy, C_1-C_4-Halogenalkyl oder mit Halogen substituiertes Benzyl darstellen.

10. Verfahren nach Anspruch 1, wobei das Ferrocenyldiphosphin der Formel II

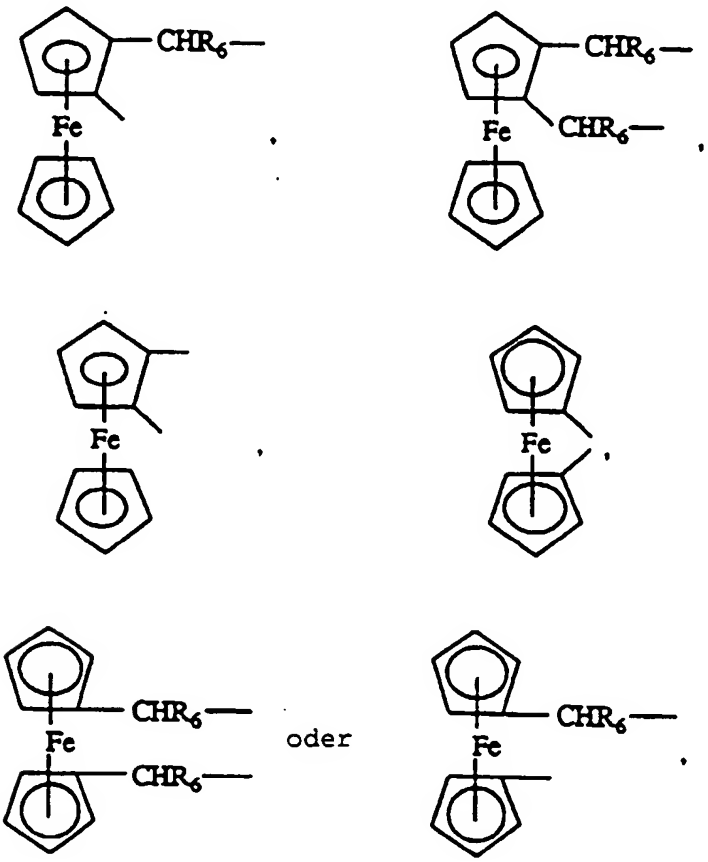
$$R_1R_2P\text{-}R_5\text{-}PR_3R_4 \qquad (II)$$

entspricht,

worin

R_1, R_2, R_3 und R_4 jeweils unabhängig voneinander einen unsubstituierten oder mit C_1-C_6-Alkyl, C_1-C_6-Alkoxy,

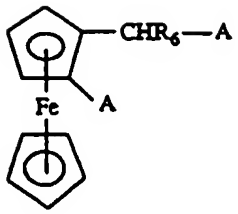
Halogen, C_1-C_6-Halogenalkyl, $(C_1$-C_{12}-Alkyl$)_3Si$, $(C_6H_5)_3Si$, C_1-C_6-Halogenalkoxy, $-NH_2$, Phenyl$_2$N-, Benzyl$_2$N-, Morpholinyl, Piperidinyl, Pyrrolidinyl, $(C_1$-C_{12}-Alkyl$)_2$N-, -Ammonium-X_1^-, $-SO_3M_1$, $-CO_2M_1$, $-PO_3M_1$, oder mit $-COO-C_1$-C_6-Alkyl substituierten Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen darstellt, worin M_1 ein Alkalimetall oder Wasserstoff darstellt und X_1^- das Anion einer einbasigen Säure darstellt;
R_1 und R_2 zusammen und R_3 und R_4 zusammen einen unsubstituierten oder mit C_1-C_6-Alkyl, C_1-C_6-Alkoxy, C_1-C_6-Halogenalkyl, C_5- oder C_6-Cycloalkyl, unsubstituiertem oder mit C_1-C_4-Alkyl, C_1-C_4-Alkoxy, C_1-C_4-Halogenalkyl oder Halogen substituiertem Phenyl oder unsubstituiertem oder mit C_1-C_4-Alkyl, C_1C_4-Alkoxy, C_1-C_4-Halogenalkyl oder mit Halogen substituiertem Benzyl substituierten C_1-C_4-Alkylenrest bilden; und
R_5 einen Rest der Formel



darstellt;
worin
R_6 Wasserstoff, C_1-C_8-Alkyl, C_1-C_4-Fluoralkyl, Phenyl oder Phenyl mit 1 bis 3 C_1-C_4-Alkyl- oder C_1-C_4-Alkoxysubstituenten darstellt.

11. Verfahren nach Anspruch 10, wobei R_1, R_2, R_3 und R_4 gleiche oder verschiedene Reste der nachstehenden Gruppe darstellen: C_1-C_6-Alkyl, Cyclopentyl und Cyclohexyl, die unsubstituiert sind oder ein bis drei C_1-C_4-Alkyl- oder C_1-C_4-Alkoxysubstituenten aufweisen; und Benzyl und insbesondere Phenyl, die unsubstituiert sind oder ein bis drei C_1-C_4-Alkyl-, C_1-C_4-Alkoxy-, F-, Cl, C_1-C_4-Fluoralkyl- oder C_1-C_4-Fluoralkoxysubstituenten aufweisen.

12. Verfahren nach Anspruch 10, wobei die Diphosphinliganden DIP jene der Formel III sind



(III)

worin

R_6 Wasserstoff und insbesondere Methyl darstellt und
A gleiche oder verschiedene Gruppen $-P(R)_2$ wiedergibt, worin R C_1-C_6-Alkyl, Cyclohexyl, Phenyl, Benzyl oder Phenyl oder Benzyl mit jeweils ein bis drei C_1-C_4-Alkyl-, disubstituierten Amino-, C_1-C_4-Alkoxy-, $-CF_3$ oder teilweise oder vollständig fluorierten C_1-C_4-Alkoxysubstituenten bedeutet.

13. Verfahren nach Anspruch 12, wobei das Diphosphin der Formel III chiral ist und R_6 C_1-C_4-Alkyl oder Phenyl oder Benzyl mit jeweils ein bis drei C_1-C_4-Alkyl- oder C_1-C_4-Alkoxysubstituenten darstellt, A gleiche oder verschiedene Gruppen $-P(R)_2$ wiedergibt, worin R verzweigtes C_3-C_6-Alkyl, Cyclohexyl, Phenyl, Benzyl oder Phenyl oder Benzyl, jeweils mit ein bis drei C_1-C_4-Alkyl-, C_1-C_4-Dialkylamino-, C_1-C_4-Alkoxy-, $-CF_3$ oder teilweise oder vollständig fluorierten C_1-C_4-Alkoxysubstituenten darstellt.

14. Verfahren nach Anspruch 13, wobei R in der Gruppe $P(R)_2$ Phenyl oder substituiertes Phenyl darstellt.

15. Verfahren nach Anspruch 1, wobei die Diphosphine ausgewählt sind aus der nachstehenden Gruppe:

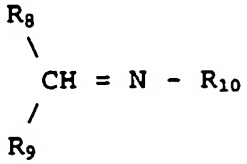
{(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]}ethyldi-(3,5-dimethyl-phenyl)phosphin
{(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]}ethyldi-(3,5-dimethyl-4-N,N-dipropylaminophenyl)phosphin
{(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]}ethyldi-(3,5-di-iso-propyl-4-N,N-dimethylaminophenyl)phosphin
{(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]}ethyldi-(3,5-di-iso-propyl-4-N,N-dibenzylylaminophenyl)phosphin
{(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]}ethyldi-(3,5-dimethyl-4-N,N-dibenzylylaminophenyl)phosphin
{(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]}ethyldi-(3,5-dimethyl-4-(1'-pyrrolo)phenyl)phosphin
{(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]}ethyldi-(3,5-dimethyl-4-N,N-dipentylaminophenyl)phosphin
{(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]}ethyldi-(3,5-dimethyl-4-N,N-dimethylaminophenyl)phosphin
{(R)-1-[(S)-2-(Di(4-methoxyphenyl)phosphino)ferrocenyl]}ethyldi(3,5-dimethyl-4-N,N-dimethylaminophenyl)phosphin und insbesondere
{(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]}ethyl-di(3,5-dimethyl-phenyl)phosphin.

16. Verfahren nach Anspruch 1, wobei die Katalysatoren jene der Formel Ib sind

$$[(DIP)IrI_2H]_2 \qquad (Ib),$$

worin DIP wie in Anspruch 1 definiert ist.

17. Verfahren nach Anspruch 1, wobei die Imine die Formel IV aufweisen



$$\begin{array}{l} R_8 \\ \backslash \\ \quad CH = N - R_{10} \\ / \\ R_9 \end{array} \qquad (IV),$$

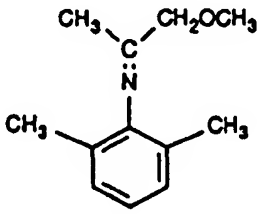
worin

R_{10} lineares oder verzweigtes C_1-C_{12}-Alkyl, Cycloalkyl mit 3 bis 8 Ringkohlenstoffatomen; Heterocycloalkyl, gebunden über ein Kohlenstoffatom und mit 3 bis 8 Ringatomen und 1 oder 2 Heteroatomen der Gruppe O, S und NR_{11}, ein über ein Alkylkohlenstoffatom gebundenes C_7-C_{16}-Aralkyl oder mit dem Cycloalkyl oder Heterocycloalkyl oder Heteroaryl substituiertes C_1-C_{12}-Alkyl bedeutet;
oder worin R_{10} C_6-C_{12}-Aryl oder über ein Ringkohlenstoff-atom gebundenes C_4-C_{11}-Heteroaryl und mit ein oder 2 Heteroatomen im Ring bedeutet; R_{10} unsubstituiertes oder mit -CN, -NO_2, F, Cl, C_1-C_{12}-Alkyl, C_1-C_{12}-Alkoxy, C_1-C_{12}-Alkylthio, C_1-C_6-Halogenalkyl, -OH, C_6-C_{12}-Aryl oder -Aryloxy oder -Arylthio, C_7-C_{16}-Aralkyl oder -Aralkoxy oder -Aralkylthio, sekundärem Amino mit 2 bis 24 Kohlenstoffatomen, -$CONR_{12}R_{13}$ oder mit -$COOR_{12}$ substituiert ist, und die Arylreste und die Arylgruppen in Aralkyl, Aralkoxy und Aralkylthio ihrerseits unsubstituiert oder mit -CN, -NO_2, F, Cl, C_1-C_4-Alkyl, -Alkoxy, -Alkylthio, -OH, -$CONR_{12}R_{13}$ oder mit -$COOR_{12}$ substituiert sind;
R_{12} und R_{13} jeweils unabhängig voneinander Wasserstoff, C_1-C_{12}-Alkyl, Phenyl oder Benzyl darstellen, oder R_{12} und R_{13} zusammen Tetra- oder Pentamethylen oder 3-Oxapentylen darstellen;
R_{11} unabhängig die gleiche Bedeutung wie für R_{12} angegeben aufweist;
R_8 und R_9 jeweils unabhängig voneinander ein Wasserstoffatom, C_1-C_{12}-Alkyl oder Cycloalkyl mit 3 bis 8 Ringkohlenstoffatomen, wobei jedes davon unsubstituiert oder mit -OH, C_1C_{12}-Alkoxy, Phenoxy, Benzyloxy, sekundärem Amino mit 2 bis 24 Kohlenstoffatomen, -$CONR_{12}R_{13}$ oder mit -$COOR_{12}$ substituiert ist; C_6-C_{12}-Aryl oder C_7-C_{16}-Aralkyl, wobei jeder davon unsubstituiert oder wie R_{10} substituiert ist, oder -$CONR_{12}R_{13}$ oder -$COOR_{12}$, worin R_{12} und R_{13} wie vorstehend definiert sind, darstellen; oder
R_{10} wie vorstehend definiert ist und R_8 und R_9 zusammen Alkylen mit 2 bis 5 Kohlenstoffatomen, das gegebenenfalls durch 1 oder 2 Reste -O-, -S- oder -NR_6- unterbrochen ist und/oder unsubstituiert oder mit =O substituiert oder wie vorstehend für R_8 und R_9 in der Bedeutung von Alkyl substituiert ist und/oder mit Benzol, Pyridin, Pyrimidin, Furan, Thiophen oder Pyrrol kondensiert ist; oder
R_9 wie vorstehend definiert ist und R_8 und R_{10} zusammen Alkylen mit 2 bis 5 Kohlenstoffatomen darstellen, das gegebenenfalls durch 1 oder 2 Reste -O-, -S- oder -NR_{11}- unterbrochen ist, und/oder unsubstituiert oder mit =O oder wie vorstehend für R_8 und R_9 in der Bedeutung von Alkyl substituiert ist und/oder mit Benzol, Pyridin, Pyrimidin, Furan, Thiophen oder Pyrrol kondensiert ist.

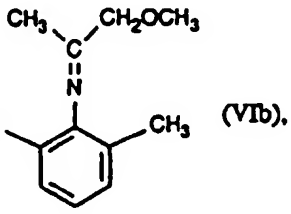
18. Verfahren nach Anspruch 17, wobei R_8 und R_9 verschieden voneinander sind.

19. Verfahren nach Anspruch 17, wobei in Formel IV R_{10} 2,6-Di-C_1-C_4-alkylphen-1-yl darstellt, R_8 C_1-C_4-Alkyl darstellt, und R_9 C_1-C_4-Alkyl, C_1-C_4-Alkoxymethyl oder C_1-C_4-Alkoxyethyl darstellt.

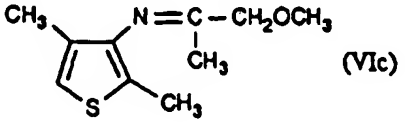
20. Verfahren nach Anspruch 17, wobei die Imine die Formeln



(VIa),



(VIb),



(VIc)

aufweisen.

21. Verfahren nach Anspruch 1, wobei das Molverhältnis von Imin-zu-Iridiumkatalysator 1 000 000:10 ist.

22. Verfahren nach Anspruch 21, wobei das Molverhältnis von Imin-zu-Iridiumkatalysator 500 000:20 ist.

23. Verfahren nach Anspruch 21, wobei das Molverhältnis von Imin-zu-Iridiumkatalysator 200 000:100 ist.

24. Verfahren nach Anspruch 21, wobei das Molverhältnis von Imin-zu-Iridiumkatalysator 100 000:100 ist.

25. Verfahren nach Anspruch 1, wobei die Reaktionstemperatur -20 bis 100°C ist.

26. Verfahren nach Anspruch 1, wobei der Wasserstoffdruck 2×10^5 bis $1{,}5 \times 10^7$ Pa ist.

27. Verfahren nach Anspruch 1, wobei die Reaktion in Gegenwart eines Lösungsmittels ausgeführt wird.

Revendications

1. Un procédé de préparation d'amines primaires ou secondaires par hydrogénation d'imines avec de l'hydrogène sous une pression élevée et en présence d'un complexe d'Ir(III) dinucléaire ayant des ligands diphosphiniques ditertiaires, des ponts halogénures, des ligands halogénures et hydrures ou un sel d'un complexe d'halogénure d'Ir(III) contenant des ligands diphosphiniques ditertiaires, comme catalyseur, où le catalyseur correspond à la formule I ou la ou aux mélanges d'au moins 2 composés de formule I, d'au moins 2 composés des formules I et Ia, ou d'au moins deux composés de formule Ia

$$[(DIP)IrX_qY_r]_2 \qquad (I),$$

$$[(DIP)X_4]^{\ominus}Me^{\oplus} \qquad (Ia),$$

où

DIP signifie le ligand diphosphinique ditertiaire d'une ferrocényldiphosphine, dont les groupes phosphine sont soit liés directement ou via un groupe formant pont $-CR_vR_w-$ dans les positions ortho du cycle cyclopentadiényle ou sont liés chacun à un cycle cyclopentadiényle d'un ferrocényle, pour former un cycle à 5, 6 ou 7 chaînons, ensemble avec l'atome Ir;
R_v et R_w signifient chacun indépendamment de l'autre, l'hydrogène, un groupe C_1-C_8alkyle, C_1-C_4fluoroalkyle, phényle ou benzyle, ou signifient un groupe phényle ou benzyle chacun ayant de 1 à 3 substituants C_1-C_4alkyle ou C_1-C_4alcoxy;
X signifie Cl, Br ou I;
Y signifie H;
q signifie un nombre 2 ou 3 et r signifie 0 ou 1, la somme q+r étant égale à 3; et
$Me^{\oplus}$ signifie un cation de métal alcalin ou un ammonium quaternaire.

2. Un procédé selon la revendication 1, où R_w signifie l'hydrogène.

3. Un procédé selon les revendications 1 et 2, où R_v signifie un groupe C_1-C_4alkyle.

4. Un procédé selon la revendication 3, où R_v signifie un groupe méthyle.

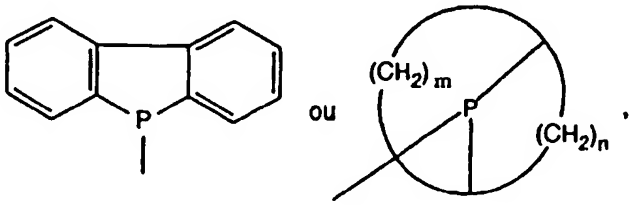
5. Un procédé selon la revendication 1, où la diphosphine ditertiaire contient au moins un groupe chiral et signifie un stéréoisomère ou une paire de diastéréoisomères.

6. Un procédé selon la revendication 1, où les groupes phosphine contiennent deux groupes hydrocarbonés identiques ou différents, non substitués ou substitués ayant de 1 à 20 atomes de carbone.

7. Un procédé selon la revendication 1, où les diphosphines contiennent deux restes identiques ou différents parmi le groupe suivant: un groupe C_1-C_{12}alkyle linéaire ou ramifié; C_5-C_{12}cycloalkyle non substitué ou substitué par un groupe C_1-C_6alkyle ou C_1-C_6alcoxy, C_5-C_{12}cycloalkyl-CH_2-, phényle et benzyle; et phényle et benzyle substi-

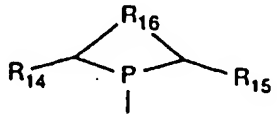
tués chacun par un halogène, un groupe C_1-C_6haloalkyle, $(C_1$-C_{12}-alkyl$)_3Si$, $(C_5H_5)_3Si$, C_1-C_6haloalcoxy, $-NH_2$, phényl$_2$N-, benzyl$_2$-N-, morpholinyle, pipéridinyle, pyrrolidinyle, $(C_1$-C_{12}alkyl$)_2$N-, -ammonium-$X_1^{\ominus}$, $-SO_3M_1$, $-CO_2M_1$, $-PO_3M_1$ ou par -COO-C_1-C_6alkyle; où M_1 signifie un métal alcalin ou l'hydrogène et $X_1^{\ominus}$ signifie l'anion d'un acide monobasique, et M_1 signifie de préférence H, Li, Na ou K.

8. Un procédé selon la revendication 1, où les groupes phosphine sont des restes de formule



où m et n signifient chacun indépendamment de l'autre, un nombre entier de 2 à 10 et la somme m+n est égale à 4 à 12.

9. Un procédé selon la revendication 1, où les groupes phosphine sont des restes de formule



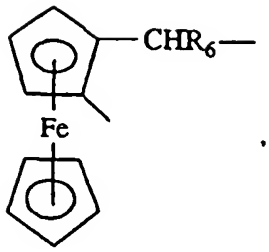
où R_{16} signifie un groupe C_1-C_4alkylène, de préférence C_2- ou C_3-alkylène, et R_{14} et R_{15} signifient chacun indépendamment de l'autre, l'hydrogène, un groupe C_1-C_6alkyle, C_1-C_6alcoxy, C_1-C_6haloalkyle, C_5- ou C_6-cycloalkyle, ou phényle qui est non substitué ou substitué par un groupe C_1-C_4alkyle, C_1-C_4alcoxy, C_1-C_4haloalkyle ou par un halogène, ou benzyle qui est non substitué ou substitué par un groupe C_1-C_4alkyle, C_1-C_4alcoxy, C_1-C_4haloalkyle ou par un halogène.

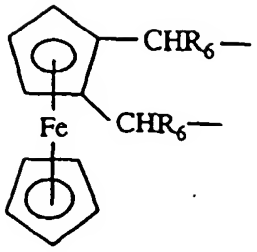
10. Un procédé selon la revendication 1, où la ferrocényldiphosphine correspond à la formule II

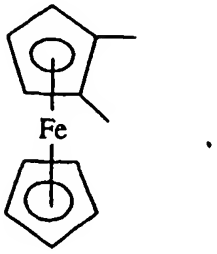
$$R_1R_2P\text{-}R_5\text{-}PR_3R_4 \qquad \text{(II)},$$

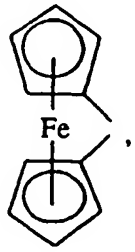
où

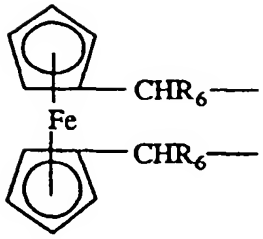
R_1, R_2, R_3 et R_4 signifient chacun indépendamment des autres, un reste hydrocarboné ayant de 1 à 20 atomes de carbone qui est non substitué ou substitué par un groupe C_1-C_6alkyle, C_1-C_6alcoxy, un halogène, un groupe C_1-C_6haloalkyle, $(C_1$-C_{12}alkyl$)_3Si$, $(C_6H_5)_3Si$, C_1-C_6haloalcoxy, $-NH_2$, phényl$_2$N-, benzyl$_2$-N-, morpholinyle, pipéridinyle, pyrrolidinyle, $(C_1$-C_{12}alkyl$)_2$N-, -ammonium-$X_1^{\ominus}$, $-SO_3M_1$, $-CO_2M_1$, $-PO_3M_1$ ou par -COO-C_1-C_6alkyle, où M_1 signifie un métal alcalin ou l'hydrogène et $X_1^{\ominus}$ signifie l'anion d'un acide monobasique;
R_1 et R_2 ensemble et R_3 et R_4 ensemble forment un reste C_1-C_4alkylène qui est non substitué ou substitué par un groupe C_1-C_6alkyle, C_1-C_6alcoxy, C_1-C_6haloalkyle, C_5-ou C_6-cycloalkyle, par un groupe phényle qui est non substitué ou substitué par un groupe C_1-C_4alkyle, C_1-C_4alcoxy, C_1-C_4haloalkyle ou par un halogène, ou par un groupe benzyle qui est non substitué ou substitué par un groupe C_1-C_4alkyle, C_1-C_4alcoxy, C_1-C_4haloalkyle ou par un halogène; et
R_5 signifie un reste de formule



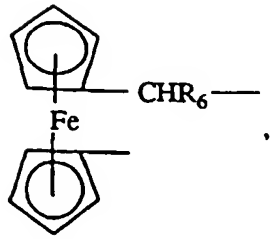








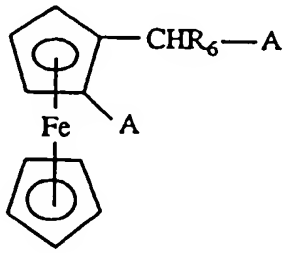
ou



où R_6 signifie l'hydrogène, un groupe C_1-C_8alkyle, C_1-C_4fluoroalkyle, phényle ou phényle ayant de 1 à 3 substituants C_1-C_4alkyle ou C_1-C_4alcoxy.

11. Un procédé selon la revendication 10, où R_1, R_2, R_3 et R_4 sont des restes identiques ou différents parmi le groupe suivant: un groupe C_1-C_6alkyle; cyclopentyle et cyclohexyle qui sont non substitués ou ont de 1 à 3 substituants C_1-C_4alkyle ou C_1-C_4alcoxy; et benzyle et spécialement phényle qui sont non substitués ou ont de 1 à 3 substituants C_1-C_4alkyle, C_1-C_4alcoxy, F, Cl, C_1-C_4fluoroalkyle ou C_1-C_4fluoroalcoxy.

12. Un procédé selon la revendication 10, où les ligands diphosphiniques DIP sont ceux de formule III



(III),

où

R_6 signifie l'hydrogène et spécialement un groupe méthyle; et
A représente des groupes identiques ou différents $-P(R)_2$, où R signifie un groupe C_1-C_6alkyle, cyclohexyle, phényle, benzyle, ou phényle ou benzyle chacun ayant de 1 à 3 substituants C_1-C_4alkyle, amino disubstitué, C_1-C_4alcoxy, $-CF_3$ ou C_1-C_4alcoxy partiellement ou complètement fluoré.

13. Un procédé selon la revendication 12, où la diphosphine de formule III est chirale et R_6 signifie un groupe C_1-C_4alkyle, ou phényle ou benzyle chacun ayant de 1 à 3 substituants C_1-C_4alkyle ou C_1-C_4alcoxy, A représente des groupes identiques ou différents $-P(R)_2$, où R signifie un groupe C_3-C_6alkyle ramifié, cyclohexyle, phényle, benzyle, ou phényle ou benzyle chacun ayant de un à trois substituants C_1-C_4alkyle, C_1-C_4dialkylamino, C_1-C_4alcoxy, $-CF_3$ ou C_1-C_4alcoxy partiellement ou complètement fluoré.

14. Un procédé selon la revendication 13, où R dans le groupe $P(R)_2$, signifie un groupe phényle ou phényle substitué.

15. Un procédé selon la revendication 1, où les diphosphines sont choisies parmi le groupe suivant:

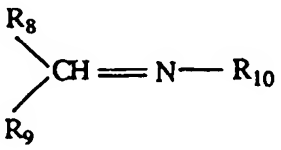
la {(R)-1-[(S)-2-(diphénylphosphino)ferrocényl]}éthyl-di(3,5-diméthyl-phényl)phosphine,
la{(R)-1-[(S)-2-(diphénylphosphino)ferrocényl]}éthyl-di(3,5-diméthyl-4-N,N-dipropylaminophényl)phosphine,
la {(R)-1-[(S)-2-(diphénylphosphino)ferrocényl]}éthyl-di(3,5-di-iso-propyl-4-N,N-diméthylaminophényl)phosphine,
la {(R)-1-[(S)-2-(diphénylphosphino)ferrocényl]}éthyl-di(3,5-di-iso-propyl-4-N,N-dibenzylylaminophényl)phosphine,
la {(R)-1-[(S)-2-(diphénylphosphino)ferrocényl]}éthyl-di(3,5-diméthyl-4-N,N-dibenzylylaminophényl)phosphine,
la {(R)-1-[(S)-2-(diphénylphosphino)ferrocényl]}éthyl-di(3,5-diméthyl-4-(1'-pyrrolo)phényl)phosphine,
la {(R)-1-[(S)-2-(diphénylphosphino)ferrocényl]}éthyl-di(3,5-diméthyl-4-N,N-dipentylaminophényl)phosphine,
la {(R)-1-[(S)-2-(diphénylphosphino)ferrocényl]}éthyl-di(3,5-diméthyl-4-N,N-diméthylaminophényl)phosphine,
la {(R)-1-[(S)-2-di(4-méthoxyphényl)phosphino)ferrocényl]}éthyl-di(3,5-diméthyl-4-N,N-diméthylaminophényl)phosphine, et spécialement
la {(R)-1-[(S)-2-(diphénylphosphino)ferrocényl]}éthyl-di(3,5-diméthyl-phényl)-phosphine.

16. Un procédé selon la revendication 1, où les catalyseurs sont ceux de formule Ib

$$[(DIP)IrI_2H]_2 \qquad (Ib)$$

où DIP est comme défini à la revendication 1.

17. Un procédé selon la revendication 1, où les imines sont des imines de formule IV



(IV),

où

R_{10} signifie un groupe C_1-C_{12}alkyle linéaire ou ramifié, cycloalkyle ayant de 3 à 8 atomes de carbone dans le cycle; un groupe hétérocycloalkyle lié via un atome de carbone et ayant de 3 à 8 atomes dans le cycle et 1 ou 2 hétéroatomes parmi le groupe O, S et NR_{11}; un groupe C_7-C_{16}aralkyle lié via un atome de carbone alkylique, ou un groupe C_1-C_{12}alkyle substitué par ledit groupe cycloalkyle ou hétérocycloalkyle ou hétéroaryle;
ou dans lequel R_{10} signifie un groupe C_6-C_{12}aryle, ou C_4-C_{11}hétéroaryle lié via un atome de carbone du cycle et ayant 1 ou 2 hétéroatomes dans le cycle; R_{10} étant non substitué ou substitué par -CN, $-NO_2$, F, Cl, un

groupe C_1-C_{12}alkyle, C_1-C_{12}alcoxy, C_1-C_{12}alkylthio, C_1-C_6haloalkyle, -OH, C_6-C_{12}aryle ou -aryloxy ou -arylthio, C_7-C_{16}aralkyle ou -aralcoxy ou -arylkylthio, amino secondaire ayant de 2 à 24 atomes de carbone, $-CONR_{12}R_{13}$ ou par $-COOR_{12}$, et les restes aryle et les groupes aryle dans les groupes aralkyle, aralcoxy et aralkylthio étant à leur tour non substitués ou substitués par -CN, $-NO_2$, F, Cl, un groupe C_1-C_4alkyle, -alcoxy, -alkylthio, -OH, $-CONR_{12}R_{13}$ ou par $-COOR_{12}$;

R_{12} et R_{13} signifient chacun indépendamment de l'autre, l'hydrogène, un groupe C_1-C_{12}alkyle, phényle ou benzyle, ou bien

R_{12} et R_{13} signifient ensemble un groupe tétra- ou penta-méthylène ou 3-oxapentylène; R_{11} indépendamment a la même signification que celle donnée pour R_{12};

R_8 et R_9 signifient chacun indépendamment de l'autre, un atome d'hydrogène, un groupe C_1-C_{12}alkyle ou cycloalkyle ayant de 3 à 8 atomes de carbone dans le cycle, chacun d'entre eux étant non substitué ou substitué par -OH, C_1-C_{12}alcoxy, phénoxy, benzyloxy, amino secondaire ayant de 2 à 24 atomes de carbone, $-CONR_{12}R_{13}$ ou par $-COOR_{12}$; un groupe C_6-C_{12}aryle ou C_7-C_{16}aralkyle chacun d'entre eux étant non substitué ou substitué comme R_{10}, ou $-CONR_{12}R_{13}$ ou $-COOR_{12}$, où R_{12} et R_{13} sont tels que définis plus haut; ou bien

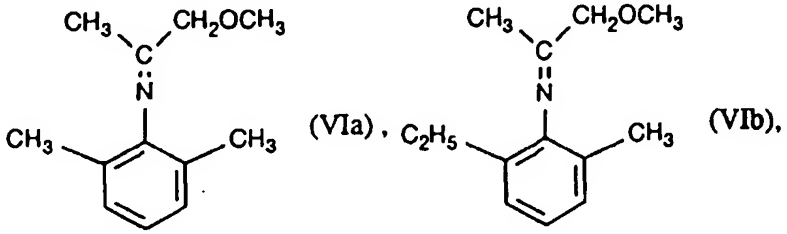
R_{10} est tel que défini plus haut et R_8 et R_9 signifient ensemble un groupe alkylène ayant de 2 à 5 atomes de carbone qui est éventuellement interrompu par 1 ou 2 restes -O-, -S- ou $-NR_6$-, et/ou non substitué ou substitué par =O ou comme indiqué plus haut pour R_8 et R_9 dans la signification du groupe alkyle, et/ou condensé avec les groupes benzène, pyridine, pyrimidine, furanne, thiophène ou pyrrole; ou bien

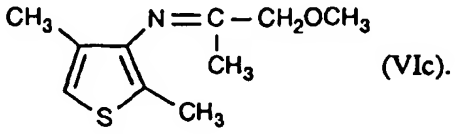
R_9 est tel que défini plus haut et R_8 et R_{10} signifient ensemble un groupe alkylène ayant de 2 à 5 atomes de carbone qui est éventuellement interrompu par 1 ou 2 restes -O-, -S- ou $-NR_{11}$, et/ou non substitué ou substitué par =O ou comme indiqué plus haut pour R_8 et R_9 dans la signification du groupe alkyle, et/ou condensé avec les groupes benzène, pyridine, pyrimidine, furanne, thiophène ou pyrrole.

18. Un procédé selon la revendication 17, où R_8 et R_9 sont différents l'un de l'autre.

19. Un procédé selon la revendication 17, où, dans la formule IV, R_{10} signifie un groupe 2,6-di-C_1-C_4alkyl-phen-1-yle, R_8 signifie un groupe C_1-C_4alkyle, et R_9 signifie un groupe C_1-C_4alkyle, C_1-C_4alcoxyméthyle ou C_1-C_4alcoxyéthyle.

20. Un procédé selon la revendication 17, où les imines sont des imines des formules





21. Un procédé selon la revendication 1, où le rapport molaire de l'imine au catalyseur d'iridium est de 1 000 000 à 10.

22. Un procédé selon la revendication 21, où le rapport molaire de l'imine au catalyseur d'iridium est de 500 000 à 20.

23. Un procédé selon la revendication 21, où le rapport molaire de l'imine au catalyseur d'iridium est de 200 000 à 100.

24. Un procédé selon la revendication 21, où le rapport molaire de l'imine au catalyseur d'iridium est de 100 000 à 100.

25. Un procédé selon la revendication 1, où la température de réaction est comprise entre -20 et 100°C.

26. Un procédé selon la revendication 1, où la pression d'hydrogène est comprise entre 2×10^5 et $1,5 \times 10^7$ Pa.

27. Un procédé selon la revendication 1, où la réaction est effectuée en présence d'un solvant.